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(54) RESIN COMPOSITION AND LAMINATE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a resin composition which has melt flowability required on a molding processing and adhesivity to polyurethane foams in an excellent balance and can give a laminate strongly adhered to the polyurethane without using a primer (adhesive), and to provide the laminate obtained using the resin composition.

SOLUTION: This resin composition comprising (A) 100 pts.wt. of a copolymer comprising an epoxy group-containing monomer and an α -olefin and (B) 3 to 100 pts.wt. of a terpene-phenolic copolymer, and the laminate obtained by laminating the layer of the resin composition to the layer of a polyurethane.

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CLAIMS

[Claim(s)]

[Claim 1] the following -- a component -- (-- A --) -- 100 -- weight -- the section -- and -- a component -- (-- B --) -- three - 100 -- weight -- the section -- containing -- resin -- a constituent .

(A): The copolymer which consists of an epoxy group content monomer and an alpha olefin (B) : terpene-phenol copolymer [claim 2] being according to claim 1 -- (-- A --) -- 100 -- weight -- the section -- (-- B --) -- three - 100 -- weight -- the section -- and -- the following -- a component -- (-- C --) -- three - 80 -- weight -- the section -- containing -- resin -- a constituent .

(C): Hydroxyl-group content copolymers other than a component (B) [claim 3] Resin constituent powder for powder molding which it consists of a resin constituent according to claim 1 or 2, and is the mean particle diameter of 30-1000 micrometers.

[Claim 4] The layered product which comes to carry out the laminating of the layer (1) of a resin constituent according to claim 1 or 2, and the layer (2) of polyurethane (I).

[Claim 5] The layered product which comes to carry out the laminating of the layer (1) of a resin constituent according to claim 1 or 2, and the layer (3) of thermoplastic elastomer (II).

[Claim 6] The manufacture approach of a layered product that a layered product (II) according to claim 5 is manufactured by dry powder pressing.

[Claim 7] The layered product which comes to carry out the laminating of the layer (3) of thermoplastic elastomer, the layer (1) of a resin constituent according to claim 1 or 2, and the layer (2) of polyurethane one by one (III).

[Claim 8] The layered product which comes to carry out the laminating of the layer (3) of thermoplastic elastomer, the layer (1) of a resin constituent according to claim 1 or 2, the layer (2) of polyurethane, and the thermoplastics center layer (4) one by one (IV).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a resin constituent and a layered product. Furthermore, in detail, this invention is excellent in the adhesive balance of the melting fluidity and polyurethane foam which are called for at the time of fabrication, and it relates to the layered product obtained using the resin constituent and this resin constituent which can obtain polyurethane and the layered product pasted up firmly, without using a primer (adhesives).

[0002]

[Description of the Prior Art] For example, the layered product of resin is used abundantly at the interior parts of an automobile. Usually, as this layered product, what carried out the laminating of the epidermis layer for making an appearance good was used for the polyurethane foaming layer for discovering cushioning properties, and vinyl chloride resin has been used widely as this epidermis layer. However, the inclination for vinyl chloride resin to be kept at arm's length becomes strong from a viewpoint of environmental protection in recent years, and an ingredient which replaces vinyl chloride resin is desired. Research using thermoplastic elastomer as this ingredient is advanced. However, according to the Prior art, the adhesive property of thermoplastic elastomer and polyurethane was inadequate, and in order to obtain a firm layered product, to use a primer (adhesives) was needed. However, the technique using a primer has the problem that work environment gets worse with the organic solvent contained in a primer besides complicated-izing of the process accompanying the cost rise for a primer, and the spreading process of a primer.

[0003]

[Problem(s) to be Solved by the Invention] In this present condition, the technical problem which this invention tends to solve is excellent in the adhesive balance of the melting fluidity and polyurethane foam which are called for at the time of fabrication, and it is related with the layered product obtained using the resin constituent and this resin constituent which can obtain polyurethane and the layered product pasted up firmly, without using a primer (adhesives).

[0004]

[Means for Solving the Problem] namely, -- this invention -- inside -- one -- invention -- the following -- a component -- (-- A --) -- 100 -- weight -- the section -- and -- a component -- (-- B --) -- three - 100 -- weight -- the section -- containing -- resin -- a constituent -- starting -- a thing -- it is .

(A): The copolymer which consists of an epoxy group content monomer and an alpha olefin (B) : other invention relates to the layered product (I) which comes to carry out the laminating of the layer (1) of the above-mentioned resin constituent, and the layer (2) of polyurethane among a terpene-phenol copolymer and this invention.

[0005]

[Embodiment of the Invention] The component (A) of this invention is a copolymer which consists of an

epoxy group content monomer and an alpha olefin. The copolymer which consists of an epoxy group content monomer and an alpha olefin is a copolymer of the monomer and alpha olefin which have an epoxy ring, and glycidyl acrylate, glycidyl methacrylate, vinyl glycidyl ether, allyl glycidyl ether, methacrylic glycidyl ether, itaconic-acid glycidyl ester, etc. are raised as an example of the monomer which has an epoxy ring.

[0006] Ethylene, a propylene, 1-butene, etc. are raised as an example of an alpha olefin.

[0007] Although the copolymer which consists of an epoxy group content monomer and an alpha olefin is a copolymer of the monomer and alpha olefin which have an epoxy ring, the monomer which has an epoxy ring, and monomers other than an alpha olefin also contain that by which copolymerization is carried out.

[0008] As the monomer which has an epoxy ring, and monomers other than an alpha olefin, acrylate, such as vinyl aromatic compounds, such as vinyl ketones, such as carboxylic-acid vinyl ester, such as vinyl acetate and propionic-acid vinyl, a methyl vinyl ketone, and an ethyl vinyl ketone, styrene, alpha methyl styrene, and vinyltoluene, methyl acrylate, ethyl acrylate, propylacrylate, n butyl acrylate, n octyl acrylate, methoxymethyl acrylate, and methoxy ethyl acrylate, can be raised.

[0009] The component (B) of this invention is a terpene-phenol copolymer. As a terpene, polyterpenes, such as diterpenes, such as sesquiterpenes, such as monoterpenes, such as hemiterpenes, such as an isoprene, an alpha pinene, beta pinene, and a limonene, and RONGIFOREN, and rosin, carotene, polyisoprene rubber, and natural rubber, etc. can be raised. As a phenol, trivalent phenols, such as dihydric phenol, such as univalent phenols, such as hydroxybenzene, a naphthol, an anthrol, cresol, and Timor, a catechol, resorcinol, a hydroquinone, orcin, urushiol, bisphenol A, binaphthol, and anthrahydroquinone, pyrogallol, phloroglucine, and hydroxyhydroquinone, can be raised.

[0010] In the resin constituent of this invention, (A) 100 weight section and the 3 - 100 weight section are used, and 5 - 70 weight section is used preferably. An adhesive property with polyurethane becomes that (B) is [too little / ((A) is excessive)] inadequate, and the mechanical strength of the constituent obtained as (B) is excess (too little [(A)]) on the other hand falls.

[0011] In addition to (A) which is an indispensable component, and (B), in this invention, the following (C) and/or (D) may be used.

(C): Hydroxyl-group content copolymers other than a component (B) (D) : a component (A) and olefin system polymers other than (B) [0012] As (C), they are polyvinyl alcohol and alpha olefin. - A vinyl alcohol copolymer etc. can be illustrated. Ethylene, a propylene, 1-butene, etc. can be illustrated as alpha olefin.

[0013] Per [3] (A) 100 weight section - 80 weight sections are desirable still more desirable, and the amount of (C used) is 5 - 70 weight section. The flexibility of a constituent in which (C) may become [too little] for

an adhesive property with polyurethane to be inadequate, and (C) is obtained on the other hand as it is excessive may fall.

[0014] An olefin system polymer can be illustrated as (D). As an olefin system system polymer, the copolymer which consists of alpha olefins other than polypropylene, low density polyethylene, straight chain-like low density polyethylene, ethylene, and ethylene, the copolymer which serves as ethylene and ethylene other than an alpha olefin from a copolymerizable monomer can be illustrated. As ethylene other than an alpha olefin, and a copolymerizable monomer, acrylate, such as vinyl aromatic compounds, such as vinyl ketones, such as carboxylic-acid vinyl ester, such as vinyl acetate and propionic-acid vinyl, a methyl vinyl ketone, and an ethyl vinyl ketone, styrene, alpha methyl styrene, and vinyltoluene, methyl acrylate, ethyl acrylate, propylacrylate, n butyl acrylate, n octyl acrylate, methoxymethyl acrylate, and methoxy ethyl acrylate, can be illustrated.

[0015] Per [5] (A) 100 weight section - the 500 weight sections are desirable still more desirable, and the amount of (D used) is the 10 - 300 weight section. Adhesive strength with a thermoplastic-elastomer layer may be inferior in the constituent with which (D) was obtained as too little, and, on the other hand, (D) may become excessive for an adhesive property with polyurethane to be inadequate.

[0016] What is necessary is just to carry out melting kneading of (C) and/or the (D) according to (A) and (B),

and a list for **, in order to obtain the resin constituent of this invention.

[0017] The layered product (I) of this invention is a layered product which comes to carry out the laminating of the layer (1) of the resin constituent of this invention, and the layer (2) of polyurethane. one side of the sex metal mold of the pair for polyurethane layer shaping after fabricating the layer (1) of a resin constituent by well-known approaches, such as dry powder pressing, an extrusion-molding method, compression forming, the calender fabricating method, an injection-molding method, and a vacuum-forming method, in order to obtain a layered product (I) for example, -- the layer (1) of a resin constituent -- setting -- the raw material of polyurethane -- impregnation and eye a mold clamp -- what is necessary is to make it foam and harden and just to fabricate a polyurethane foaming layer

[0018] The layered product (II) of this invention is a layered product which comes to carry out the laminating of the layer (1) of the resin constituent of this invention, and the layer (3) of thermoplastic elastomer. As thermoplastic elastomer, it is [0019]. An olefin system, a styrene system, an ester system, an urethane system, etc. can be illustrated. The olefin system and styrene system which are excellent in physical-properties balance including durable physical properties, such as thermal resistance and lightfastness, especially are desirable. Thermoplastic elastomer olefin is thermoplastic elastomer which consists of olefin system resin and olefin system rubber, and is classified into a blend type, the bridge formation type which constructed the bridge in the rubber part according to dynamic bridge formation, and a polymerization type. A styrene thermoplastic elastomer has further block copolymers, such as styrene-styrene butadiene rubber and styrene-isoprene-styrene, and these water garnishes, and the thing that carried out the compound of these block copolymers and the polyolefin resin.

[0020] What is necessary is just to fabricate by well-known approaches, such as dry powder pressing, an extrusion-molding method, compression forming, the calender fabricating method, an injection-molding method, and a vacuum-forming method, in order to obtain a layered product (II).

[0021] For example, what is necessary is just to fabricate by a powder slush molding method, the fluidized bed coating process, electrostatic spray painting, the powder spraying process, a powder rotational casting method, etc., in order to obtain a layered product (II) by dry powder pressing.

[0022] In order to obtain a layered product (II) by dry powder pressing, resin constituent powder with a mean particle diameter of 30-1000 micrometers is used for the resin constituent of this invention.

[0023] Mean particle diameter is 50-700 micrometers preferably. In case the blocking resistance of resin constituent powder falls as too little [a mean diameter] and a mean diameter carries out powder molding to it being excessive on the other hand, the melting nature of a resin constituent falls.

[0024] As an example of the approach of obtaining resin constituent powder, an extruder is used and it is pellet **** of a resin constituent by melting kneading. Subsequently, the pellet of the obtained resin constituent can be cooled (it cools below to the glass transition temperature of a resin constituent preferably), and resin constituent powder can be obtained using an impact type pulverizer.

[0025] In order to raise the blocking resistance of the obtained resin constituent powder further, it is desirable that mean particle diameter carries out 0.1-10 weight section combination of the detailed powder object 10 micrometers or less to resin constituent 100 heavy lift.

[0026] Mean particle diameter can use a powdered pigment, an alumina, a silica, an alumina silica, a calcium carbonate, etc. as a detailed powder object 10 micrometers or less.

[0027] For example, a powder slush molding method is performed by the approach of consisting of the ninth process from the first process shown below.

The first process : on the shaping side of the metal mold heated more than the melting temperature of the powder of the second process [of a process]:thermoplastic-elastomer constituent which applies a fluorine and/or a silicon system release agent on the shaping side of metal mold The third process of a process which supplies the powder of a thermoplastic-elastomer constituent : Predetermined carries out time amount heating of the powder of a thermoplastic-elastomer constituent on the shaping side of the second process. The fourth

process of a process to which welding of the powder of each other which the front face fused at least is carried out : after carrying out predetermined time progress in the third process Predetermined carries out time amount heating of the powder of the resin constituent of this invention on the shaping side of the fifth process. fifth process [of a process]: which collects the powder of the thermoplastic-elastomer constituent which was not welded -- sixth process [of a process]: which supplies the powder of the resin constituent of this invention on the shaping side of the metal mold which the powder of a thermoplastic-elastomer constituent welded -- The process to which welding of the powder of each other which the front face fused at least is carried out.

seventh process: -- the process eighth which collects the powder of the resin constituent of this invention which was not welded after carrying out predetermined-time progress in the sixth process -- ninth process [of a process]: which heats further the metal mold with which the powder of the fused thermoplastic-elastomer constituent and the powder of the resin constituent of this invention have got if needed [process:] -- the process [0028] which removes the Plastic solid which cooled metal mold after the eighth process and was formed on it from metal mold As a thermoplastic-elastomer constituent used for this powder slush molding, what is proposed by JP,5-5050,A, JP,10-30036,A, etc. is used preferably.

[0029] The layered product (III) of this invention is a layered product which comes to carry out the laminating of the layer (3) of thermoplastic elastomer, the layer (1) of the resin constituent of this invention, and the layer (2) of polyurethane one by one. Here, "it is a laminating one by one" does not show the chronological sequence of the process of a laminating, and it expresses the structure of a layered product (it is the same hereafter.). one side of the sex metal mold of the pair for polyurethane layer shaping after fabricating a layered product (II) by well-known approaches, such as dry powder pressing, an extrusion-molding method, compression forming, the calender fabricating method, an injection-molding method, and a vacuum-forming method, in order to obtain a layered product (III) for example, -- a layered product (II) -- setting -- the raw material of polyurethane -- impregnation and eye a mold clamp -- what is necessary is to make it foam and harden and just to fabricate a polyurethane foaming layer

[0030] The layered product (IV) of this invention is a layered product which comes to carry out the laminating of the layer (3) of thermoplastic elastomer, the layer (1) of the resin constituent of this invention, the layer (2) of polyurethane, and the thermoplastics center layer (4) one by one. the thermoplastics center layer which the sex metal mold of the pair for polyurethane layer shaping was alike, respectively, and was fabricated by the layered product (II), injection molding, etc. in order to have obtained the layered product (IV) -- setting -- the raw material of polyurethane -- impregnation and eye a mold clamp -- what is necessary is to make it foam and harden and just to fabricate a polyurethane foaming layer

[0031] The layered product of this invention can be used the the best for automobile interior parts, such as an instrument panel, a door trim, a console box, and a pillar, etc.

[0032]

[Example] Hereafter, although an example explains this invention to a detail, this invention is not limited to these examples.

the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 18 % of the weight of contents of example 1 glycidyl methacrylate, and 1 % of the weight of contents of vinyl acetate 190-degree-C70 weight section and a terpene-phenol copolymer (the Yasuhara Chemical make --) the YP-902 30 weight section and an anti-oxidant (the product made from tiba speciality KEMIKARUZU --) After kneading the IRGANOX1076 0.1 weight section for 5 minutes on condition that 190 degrees C and 50rpm using a lab PURASUTO mill (Product made from an Oriental energy machine, form 65C150), the press-forming machine heated by 190 degrees C performed heating for 5 minutes, and compression, and the shaping sheet of 1mm thickness was obtained. the obtained shaping sheet -- polyurethane foaming -- public funds -- the above-mentioned polyurethane foaming after setting to a mold and mixing the raw material liquid (the mixture and the polymeric MDI which consist of the propylene oxide of a glycerol, the polyol which made the ethylene

oxide addition product the subject, water, triethanolamine, triethylenediamine, etc.) of polyurethane with a high-speed agitator for 10 seconds -- public funds -- after supplying and mold clamp carrying out to a mold, it was made to foam and harden and the layered product was obtained. The layered product was cut to 50mm width of face after neglect one whole day and night, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 1.

[0033] the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 18 % of the weight of contents of example 2 glycidyl methacrylate, and 1 % of the weight of contents of vinyl acetate 190-degree-C70 weight section and a terpene-phenol copolymer (the Yasuhara Chemical make --) the YP-902 10 weight section and polyvinyl alcohol (Kuraray Co., Ltd. Make --) the CP-1210 20 weight section and an anti-oxidant (the product made from tiba speciality KEMIKARUZU --) After kneading the IRGANOX1076 0.1 weight section for 5 minutes on condition that 190 degrees C and 50rpm using a lab PURASUTO mill (Product made from an Oriental energy machine, form 65C150), the press-forming machine heated by 190 degrees C performed heating for 5 minutes, and compression, and the shaping sheet of 1mm thickness was obtained. The layered product was hereafter obtained like the example 1, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 1.

[0034] the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 18 % of the weight of contents of example 3 glycidyl methacrylate, and 1 % of the weight of contents of vinyl acetate 190-degree-C70 weight section and a terpene-phenol copolymer (the Yasuhara Chemical make --) the YP-902 10 weight section and an ethylene-vinylalcohol copolymer (Kuraray Co., Ltd. Make --) the EP-E105B20 weight section and an anti-oxidant (the product made from tiba speciality KEMIKARUZU --) After kneading the IRGANOX1076 0.1 weight section for 5 minutes on condition that 190 degrees C and 50rpm using a lab PURASUTO mill (Product made from an Oriental energy machine, form 65C150), the press-forming machine heated by 190 degrees C performed heating for 5 minutes, and compression, and the shaping sheet of 1mm thickness was obtained. The layered product was hereafter obtained like the example 1, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 1.

[0035] the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 18 % of the weight of contents of example 4 glycidyl methacrylate, and 1 % of the weight of contents of vinyl acetate 190-degree-C40 weight section and a terpene-phenol copolymer (the Yasuhara Chemical make --) the YP-902 20 weight section and an ethylene-vinylacetate copolymer (the Sumitomo Chemical [Co., Ltd.] Co., Ltd. make --) the SUMITETO HC-10 40 weight section and an anti-oxidant (the product made from tiba speciality KEMIKARUZU --) After kneading the IRGANOX1076 0.1 weight section for 5 minutes on condition that 190 degrees C and 50rpm using a lab PURASUTO mill (Product made from an Oriental energy machine, form 65C150), the press-forming machine heated by 190 degrees C performed heating for 5 minutes, and compression, and the shaping sheet of 1mm thickness was obtained. The layered product was hereafter obtained like the example 1, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 1.

[0036] the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 18 % of the weight of contents of example of comparison 1 glycidyl methacrylate, and 1 % of the weight of contents of vinyl acetate 190-degree-C70 weight section and polyvinyl alcohol (Kuraray Co., Ltd. Make --) the CP-1210 30 weight section and an anti-oxidant (the product made from tiba speciality KEMIKARUZU --) After kneading the IRGANOX1076 0.1 weight section for 5 minutes on condition that 190 degrees C and 50rpm using a lab PURASUTO mill (Product made from an Oriental energy machine, form 65C150), the press-forming machine heated by 190 degrees C performed heating for 5 minutes, and compression, and the shaping sheet of 1mm thickness was obtained. The layered product was hereafter obtained like the example 1, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 1.

[0037] The press-forming machine heated by 190 degrees C in the ethylene-glycidyl methacrylate-vinyl

acetate copolymer (MFR340g/10min, 190 degrees C) of 18 % of the weight of contents of example of comparison 2 glycidyl methacrylate and 1 % of the weight of contents of vinyl acetate performed heating for 5 minutes, and compression, and the shaping sheet of 1mm thickness was obtained. The layered product was hereafter obtained like the example 1, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 1.

[0038] 18 % of the weight of contents of example 5 [manufacture of resin constituent powder] glycidyl methacrylate, the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 1 % of the weight of contents of vinyl acetate 190-degree-C80 weight section and a terpene-phenol copolymer (the Yasuhara Chemical make --) the YP-902 20 weight section and an anti-oxidant (the product made from tibia speciality KEMIKARUZU --) The IRGANOX1076 0.1 weight section was kneaded at 110 degrees C using the 2 shaft extruder (the Japan Steel Works [, Ltd.], Ltd. make, form TEX-30SS-40W-3V), the resin constituent was obtained, it judged in the pelletizer and the pellet was obtained. This pellet was ground maintaining a cooling condition after cooling at -100 degrees C using liquid nitrogen, and the powder of a resin constituent was obtained. Resin constituent powder **** with which the resin constituent powder 100 weight section obtained in this way, the silica (Degussa AG make, OX-50) 3 weight section, and the alumina silica (Mizusawa chemistry company make, JC-30) 3 weight section were mixed for 2 minutes by the room temperature and 1500rpm using the super mixer (the Kawada factory company make, 5L super mixer), and the detailed powder object was blended.

[0039] [Manufacture of thermoplastic-elastomer constituent powder] propylene-ethylene copolymer resin (5 % of the weight of ethylene unit contents) MFR228g / 10 minutes (JIS K7210 (2.16kg of loads)) The temperature of 230 degrees C 40 weight section, the water garnish of Butadiene Styrene (MFR30g / 10 minutes (JIS K7210 (2.16kg of loads))) the temperature of 230 degrees C 45 weight section, and ethylene-propylene copolymer rubber (the Sumitomo Chemical Co., Ltd. make --) V0141 and 27 % of the weight MFR1g of SPO propylene unit contents / 10 minutes (JIS K7210 (2.16kg of loads)) the temperature of 190 degrees C 12 weight section, and a micro crystallin wax (the NIPPON SEIRO CO., LTD. make --) The HiMic10803 weight section and the anti-oxidant (product [made from tibia speciality KEMIKARUZU], IRGANOX-1076) 0.5 weight section were kneaded at 150 degrees C using the 2 shaft extruder, and the pellet of thermoplastic elastomer was obtained. This pellet was ground after cooling at -120 degrees C using liquid nitrogen, with the cooling condition maintained, and thermoplastic-elastomer constituent powder was obtained. Thermoplastic-elastomer constituent powder **** with which the thermoplastic-elastomer constituent powder 100 weight section obtained in this way, the silica (Degussa AG make, OX-50) 1 weight section, and the alumina silica (Mizusawa chemistry company make, JC-30) 2 weight section were mixed for 2 minutes by the room temperature and 1500rpm using the super mixer (the Kawada factory company make, 5L super mixer), and the detailed powder object was blended.

[0040] The powder of [manufacture of layered product which consists of layer [of the resin constituent by the powder slush molding method], and layer of thermoplastic elastomer] thermoplastic-elastomer constituent It supplies on the shaping side of the metal mold with a crimp pattern (30cm angle) heated by 260 degrees C. After leaving it for 5 seconds, excessive powder was discarded, after supplying resin constituent powder to the metal mold side where the powder of a thermoplastic-elastomer constituent adhered and leaving it for 10 seconds subsequently, excessive powder was discarded and metal mold was left for 30 seconds within 260-degree C oven. Then, the layered product which consists of a layer of a resin constituent and a layer of thermoplastic elastomer was obtained by cooling the metal mold fused in the shape of [which consists of a thermoplastic-elastomer constituent layer and a resin constituent layer] a sheet, and unmolding a sheet from this metal mold. The shaping sheet thickness obtained by the powder slush molding method was about 1mm.

[0041] The appearance from which a resin constituent stratification plane becomes a polyurethane foaming layer and a layer continuation about the shaping sheet obtained by the [manufacture of layered product to which laminating of polyurethane foaming layer was carried out] above-mentioned powder slush molding

method, polyurethane foaming -- public funds -- a mold -- setting -- the raw material liquid (the propylene oxide of a glycerol --) of polyurethane The polyol which made the ethylene oxide addition product the subject, water, triethanolamine, After mixing the mixture and the polymeric MDI which consist of triethylenediamine etc. with a high-speed agitator for 10 seconds, After supplying and mold clamp carrying out to the above-mentioned metal mold for polyurethane foaming, it was made to foam and harden and the layered product the layer of thermoplastic elastomer, the layer of a resin constituent, and a polyurethane foaming layer come to carry out a laminating one by one was obtained. The layered product was cut to 25mm width of face after neglect one whole day and night, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 2.

[0042] 18 % of the weight of contents of example 6 [manufacture of resin constituent powder] glycidyl methacrylate, the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/-- 10 min) of 1 % of the weight of contents of vinyl acetate 190-degree-C50 weight section and a terpene-phenol copolymer (the Yasuhara Chemical make --) the YP-902 20 weight section and polyvinyl alcohol (Kuraray Co., Ltd. Make --) the CP-1210 20 weight section and ethylene propylene rubber (the Sumitomo Chemical [Co., Ltd.] Co., Ltd. make --) the SPO V0141 10 weight section and an anti-oxidant (the product made from tiba speciality KEMIKARUZU --) The IRGANOX1076 0.1 weight section was kneaded at 180 degrees C using the 2 shaft extruder (the Japan Steel Works [, Ltd.], Ltd. make, form TEX-30SS-40W-3V), the resin constituent was obtained, it judged in the pelletizer and the pellet was obtained. This pellet was ground maintaining a cooling condition after cooling at -100 degrees C using liquid nitrogen, and the powder of a resin constituent was obtained. Resin constituent powder **** with which the resin constituent powder 100 weight section obtained in this way, the silica (Degussa AG make, OX-50) 3 weight section, and the alumina silica (Mizusawa chemistry company make, JC-30) 3 weight section were mixed for 2 minutes by the room temperature and 1500rpm using the super mixer (the Kawada factory company make, 5L super mixer), and the detailed powder object was blended.

[0043] The powder slush molding sheet the layer of thermoplastic elastomer, the layer of a resin constituent, and a polyurethane foaming layer come to carry out a laminating one by one was obtained like [manufacture of layered product to which laminating of shaping sheet and polyurethane foaming layer by powder slush molding method was carried out] example 5. The layered product was cut to 25mm width of face after neglect one whole day and night, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 2.

[0044] The pellet of the ethylene-glycidyl methacrylate-vinyl acetate copolymer (MFR340g/10min, 190 degrees C) of 18 % of the weight of contents of example of comparison 3 glycidyl methacrylate and 1 % of the weight of contents of vinyl acetate was ground maintaining a cooling condition after cooling at -100 degrees C using liquid nitrogen, and the powder of an ethylene-glycidyl methacrylate-vinyl acetate copolymer was obtained.

[0045] The layered product the layer of thermoplastic elastomer, the layer of the ethylene-glycidyl methacrylate-vinyl acetate copolymer obtained by the above, and a polyurethane foaming layer come to carry out a laminating one by one like [manufacture of layered product to which laminating of shaping sheet and polyurethane foaming layer by powder slush molding method was carried out] example 4 was obtained. The layered product was cut to 25mm width of face after neglect one whole day and night, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 3.

[0046] After supplying the powder of an example of comparison 4 [manufacture of thermoplastic-elastomer sheet] thermoplastic-elastomer constituent on the shaping side of the metal mold with a crimp pattern (30cm angle) heated by 260 degrees C and leaving it for 12 seconds, excessive powder was discarded and metal mold was left for 60 seconds within 260-degree C oven. Then, the powder slush molding sheet which consists of thermoplastic elastomer was obtained by cooling the metal mold fused in the shape of [which consists of a thermoplastic-elastomer constituent layer] a sheet, and unmolding a sheet from this metal mold. The

thickness of the shaping sheet obtained by the powder slush molding method was about 1mm. The primer (adhesives) (the Tokushu Shikiryō Color & Chemicals [, INC.], INC. make, AD-471) was applied to one side of the obtained thermoplastic-elastomer sheet. The appearance from which a primer spreading side becomes a polyurethane foaming layer and a layer continuation about the shaping sheet obtained by the describing [above] powder slush molding method, polyurethane foaming -- public funds -- a mold -- setting -- the raw material liquid (the propylene oxide of a glycerol --) of polyurethane The polyol which made the ethylene oxide addition product the subject, water, triethanolamine, the above-mentioned polyurethane foaming after mixing the mixture and the polymeric MDI which consist of triethylenediamine etc. with a high-speed agitator for 10 seconds -- public funds -- after supplying and mold clamp carrying out to a mold, it was made to foam and harden and the layered product the layer and polyurethane foaming layer of thermoplastic elastomer come to carry out a laminating was obtained. The layered product was cut to 25mm width of face after neglect one whole day and night, and bond strength of a shaping sheet and a polyurethane foaming layer was measured. A result is shown in Table 3.

[0047]

[Table 1]

	実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2
エチレン・グリセロール・トリメタクリレート 酢酸ビニル共重合体	70	70	70	40	70	100
テラペンフェノール共重合体 Y P-902	30	10	10	20		
ポリビニルアルコール C P-1210		20			30	
エチレン・ビニルアルコール 共重合体 E P-E105			20			
エチレン・酢酸ビニル共重合体				40		
ポリウレタン接着強度 (g/50mm幅)	1750	275	730	740	20	10

[0048]

[Table 2]

		実施例 5	実施例 6
積層体構成	1 層目	熱可塑性 エラストマー	熱可塑性 エラストマー
	2 層目	E-GMA-VA (80) テラペンフェノール (20)	E-GMA-VA (50) テラペンフェノール (20) PVA (20) エチレン・グリセロール共重合体 (10)
	3 層目	ポリウレタン発泡	ポリウレタン発泡
ポリウレタン 接着強度 (g/25mm 幅)		560	590

[0049]

[Table 3]

		比較例 3	比較例 4
積層体構成	1 層目	熱可塑性 エラストマー	熱可塑性 エラストマー
	2 層目	E-GMA-VA (100)	なし (プライマー塗布)
	3 層目	ポリウレタン発泡	ポリウレタン発泡
ポリウレタン 接着強度 (g/25mm 幅)		2 0	3 6 0

[0050]

[Effect of the Invention] The layered product obtained by this invention using polyurethane, the resin constituent which can obtain the layered product pasted up firmly, and this resin constituent, without excelling in the adhesive balance of the melting fluidity and polyurethane foam which are called for at the time of fabrication, and using a primer (adhesives) was able to be offered as explained above.

[Translation done.]